temperature may then be eliminated by nutritional environment.

This study is in agreement that thermophilic fungi have an ubiquitous distribution. However, in the present study only such sources were explored where microbial thermogenesis itself produces temperature favouring thermophiles. Future studies in the tropics should explore surface soils and pond waters to determine the frequency of occurrence of thermophiles in such places.

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RESONANCE ENERGIES OF TRICARBONYLARENECHROMIUMS

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THE order of stability of the series of π-complexes, the chromium tricarbonyl derivatives of benzene, biphenyl and phenanthrene seems on primary considerations to depend on the π-bonds in the series. Delocalisation of π-electrons takes place extensively in these compounds as manifested by their dipole moments,[1] infrared spectra[2] and other properties.[3] In bipehnyl and phenanthrene there are neighbouring ring π-electrons and the extent of participation of such electrons in the bonding becomes important. The Effective Atomic Number (E.A.N.) rule does not permit any such participation but one of us has suggested that in molecular orbital theory the interaction of all the π-orbitals must be taken into account.[4] Thus it is possible to explain the greater stability of phenyl substituted complexes such as tricarbonyl-π-tetraphenylcyclobutadieneiron.[5] The fact that in both tricarbonyl-π-biphenylchromium and tricarbonyl-π-phenanthrenechromium planar structures are maintained[6] and that considerable delocalisation takes place in free biphenyl and phenanthrene indicates the necessity of including the interaction of all π-electrons.

In view of this, we have used semiempirical molecular orbital theory for obtaining the resonance energies of the arene-metal fragments in these complexes. The interaction of all the π-electrons of the respective arene have been included in such calculations. X-ray work has shown that the aromatic moieties in these complexes are planar[6] but there are considerable and random variations of the C–C distances. Hence planar structures are assumed for the aromatic moieties with all the C–C distances taken as $1 \cdot 39$ Å. The inter-ring bond in biphenyl is $1 \cdot 48$ Å.[7] The C–Cr distance is $2 \cdot 2$ Å, the carbon atoms being those of the ring to which the chromium is bound. Further, in the phenanthrene complex the bonding is to one of the end rings.[8]

The highest filled levels amongst the M O's of the arenes are identified with the corresponding ionisation potentials :[9]

biphenyl	$H(4a_1, 4a_1) = -8 \cdot 27$ e.v.
phenanthrene	$H(4a_1, 4a_1) = -8 \cdot 03$ e.v.

Other levels are calculated with respect to these energies. The coulomb terms are taken from Berry's spectroscopic data :[10]

$$H(4p, 4p) = -3 \cdot 86 \text{ e.v.}$$
$$H(4s, 4s) = -5 \cdot 76 \text{ e.v.}$$
$$H(3d, 3d) = -6 \cdot 76 \text{ e.v.}$$

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The group overlap integrals were calculated from tables as in earlier work.[11] An example formula for the interaction of a totally symmetric orbital and the chromium $4p_z$ orbital is

$$S(\psi, 4p_z) = \sum_{i=1}^{m} C_i \{S_i (2p_\sigma 4p_\sigma) \cos^2 \theta_i - S_i (2p_\pi 4p_\pi) \sin^2 \theta_i\}$$

where C_i is the coefficient of the i-th carbon atom in the given molecular orbital, and θ_i is the angle between the Z-axis and M-C$_i$ vector ; $m = 12$ and 14 respectively for biphenyl and phenanthrene.

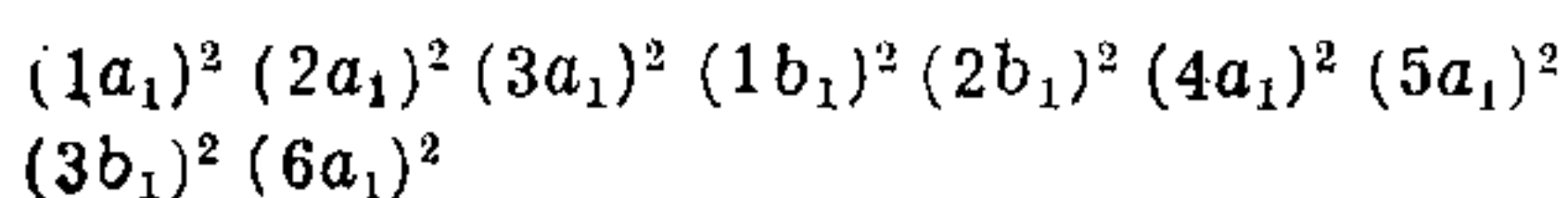The secular determinant is next set up in terms of the group overlap integrals and coulomb terms :

$$|H_{ij} - E| = 0$$

where H_{ij} is the resonance integral between the orbitals ψ_i and ψ_j and H_{ii} is the coulomb term of the orbital with 'i' and 'j' representing the different arene and chromium $3d$, $4s$, $4p$ orbitals. H_{ij} was evaluated with the assumption, $H_{ij} = kS_{ij}$, S_{ij} being the group overlap integral and for $k = 3, 5, 7, 9$ and 11 e.v.
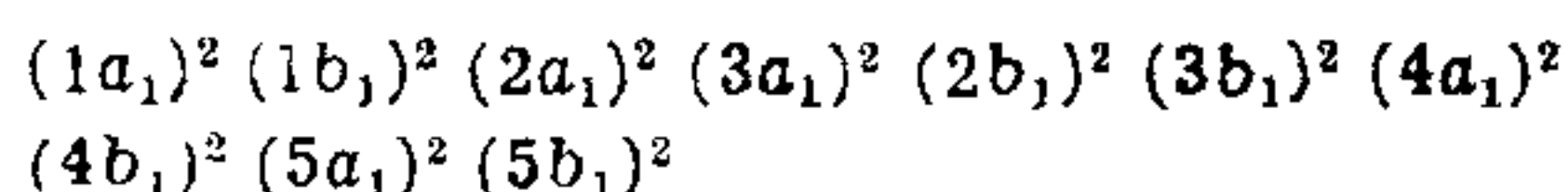
The solution in the case of biphenyl-Cr involved the solving of $14 \times 14(A_1)$ and $7 \times 7(B_1)$ matrices whereas for phenanthrene-Cr, a 23×23 matrix had to be solved. The solutions were carried out on an I.B.M. 1620 computer and the energies for the case $k = 3$ were as follows :

Biphenyl-Cr		Phenanthrene-Cr	
	e.v.		e.v.
$1a_1$	$-12 \cdot 24$	$1a_1$	$-12 \cdot 66$
$2a_1$	$-11 \cdot 25$	$1b_1$	$-11 \cdot 47$
$3a_1$	$-9 \cdot 97$	$2a_1$	$-10 \cdot 41$
$1b_1$	$-9 \cdot 12$	$3a_1$	$-9 \cdot 94$
$2b_1$	$-9 \cdot 00$	$2b_1$	$-9 \cdot 50$
$4a_1$	$-8 \cdot 43$	$3b_1$	$-8 \cdot 59$
$5a_1$	$-6 \cdot 79$	$4a_1$	$-8 \cdot 15$
$3b_1$	$-6 \cdot 76$	$4b_1$	$-6 \cdot 86$
$6a_1$	$-6 \cdot 76$	$5a_1$	$-6 \cdot 78$
		$5b_1$	$-6 \cdot 76$

The order of energies is the same for all k values and the electronic configurations of the arene-metal fragments in the two cases are biphenyl-Cr :

$$(1a_1)^2 (2a_1)^2 (3a_1)^2 (1b_1)^2 (2b_1)^2 (4a_1)^2 (5a_1)^2 (3b_1)^2 (6a_1)^2$$

phenanthrene-Cr :

$$(1a_1)^2 (1b_1)^2 (2a_1)^2 (3a_1)^2 (2b_1)^2 (3b_1)^2 (4a_1)^2 (4b_1)^2 (5a_1)^2 (5b_1)^2$$

The resonance energies are as given below. The resonance energies for benzene-Cr[12] are also given :

k	Biphenyl-Cr (e.v.)	Phenanthrene-Cr (e.v.)	Benzene-Cr (e.v.)
3	$3 \cdot 21$	$4 \cdot 02$	$3 \cdot 82$
5	$5 \cdot 04$	$6 \cdot 86$	$6 \cdot 52$
7	$7 \cdot 27$	$10 \cdot 38$	$9 \cdot 98$
9	$10 \cdot 45$	$14 \cdot 32$	$13 \cdot 83$
11	$12 \cdot 06$	$18 \cdot 56$	$17 \cdot 97$

This gives the order as phenanthrene-Cr > benzene-Cr > biphenyl-Cr. Experimentally it has been found that the phenanthrene- and the benzene-complexes form more easily and in higher yields than the biphenyl-complex. This criterion of the ease of formation and yield is not reliable because the complexes that form easily, e.g., aniline-complex are rather unstable. Accurate measurement of the ring-metal frequency would be helpful but a conclusive assignment of the frequency is difficult. Methods of thermochemistry and photochemistry seem to be important but have not been tried for this case.

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